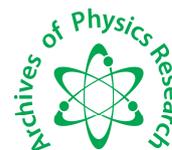




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Archives of Physics Research, 2011, 2 (3):46-50
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ISSN : 0976-0970

CODEN (USA): APRRC7

Photoluminescence studies of Eu doped Yttrium based phosphors

A. P. Zambare and K.V.R. Murthy*

Department of Physics, Agasti Arts, Commerce & D.R. Science College, Akole, Ahmednagar, (M.S.)

*Applied Physics Department, Faculty of Technology and Engineering, M. S. University of Baroda,
Baroda, India

ABSTRACT

The present paper reports Photoluminescence [PL] characteristics of Eu doped YPVO₄, Y₂O₃ and YLaVO₄ phosphors. The phosphors were prepared by adopting standard solid state reaction method. The photoluminescence emission spectra of YPVO₄: Eu³⁺ (0.5%) and Y₂O₃:Eu³⁺ (0.5%) are excited with 254 nm. Y(PV)O₄: Eu³⁺ displays PL emission at 365, 540, 561, 594 and 611 nm. Y₂O₃:Eu³⁺ displays the PL emissions at 536, 583, 589, 594, 600, 615 and 632 nm. The excitation of the Y_{0.5}LaVO₄: Eu (0.5%) phosphor with 450 nm wavelength generates a strong and broad emission in UV region i.e. 240 to 300 nm. The PL emission of Y_{0.5}LaVO₄: Eu is interesting in nature as it displays up-conversion phenomena.

Keywords : Photoluminescence, phosphors, Solid state reaction method.

Abréviations : PL: Photoluminescence, Ex: Excitation, Em: Emission

INTRODUCTION

The study of fluorescence in phosphors provides knowledge and throws light on the use of the materials as a phosphor in display and lighting devices. The study of photoluminescence properties will give the applicability of the prepared materials as display device phosphors. Although the basics of the industrial scale phosphor synthesis were well established a decade ago, the process of optimization is still continuing because of the importance of phosphor efficiency required for different applications, the production cost and hence market share. The main aim of the present investigation is to study the photoluminescence (PL) properties of Eu doped Yttrium based phosphors i.e YPVO₄, Y₂O₃ and YLaVO₄.

MATERIALS AND METHODS

In the present study all the Europium doped phosphors are synthesized by solid state diffusion reaction method at high temperature. First the high purity materials of host, activators and the fluxes are blended, mixed and then fired at 1300°C for four hours in an alumina crucible covered with a lid. The product obtained is in the form of a cake formed because of firing and sintering.

Then the cake is crushed, milled and then sorted to remove coarse and excessively crushed particles. The phosphors $\text{YPVO}_4:\text{Eu}^{3+}$, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Y}_{0.5}\text{LaVO}_4:\text{Eu}^{2+}$ are prepared and studied for their PL. The PL spectra were recorded at room temperature using the Shimadzu RF-5301 PC Spectrofluorophotometer.

RESULTS AND DISCUSSION

The photoluminescence of $\text{YPVO}_4:\text{Eu}^{3+}$ (0.5%), $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (0.5%) and $\text{Y}_{0.5}\text{LaVO}_4:\text{Eu}$ (0.5%) are presented in Fig.1,2 and 3. The intensities of the emission as well as excitation bands are given in real units in Table: 1 for better understanding. Figure.1: shows the photoluminescence spectra of $\text{Y}(\text{PV})\text{O}_4:\text{Eu}^{3+}$ (0.5%) being excited with 254 nm. The excitation of the material with 254 nm wavelength generates emission at 365, 540, 561, 594 and 611 nm. The intensity of peak at 365 nm is relatively very low as compared to 594 and 611 nm peaks. The PL emission at 594 and 611 nm are very sharp and strong. The luminescence lines at 594 and 611 nm corresponds to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (orange red) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (red) transitions of Eu. Both the observed lines are being used as red lines in lamps.

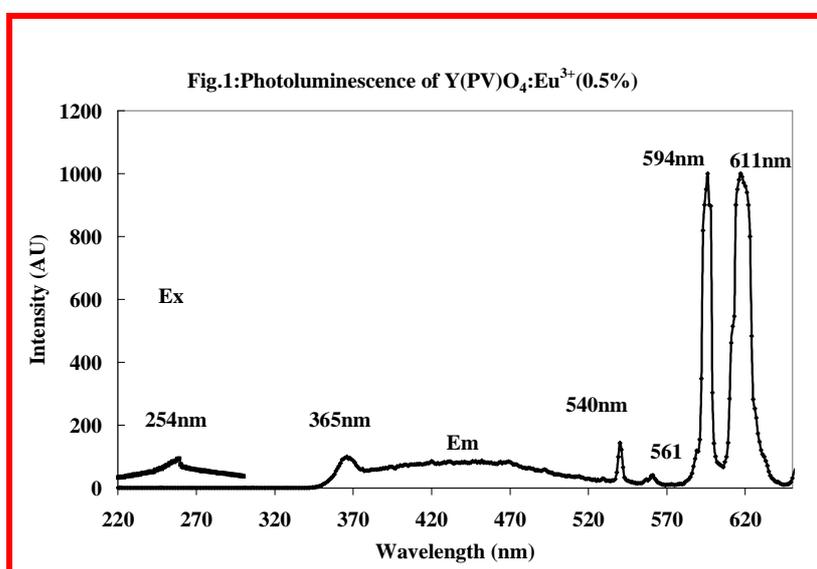
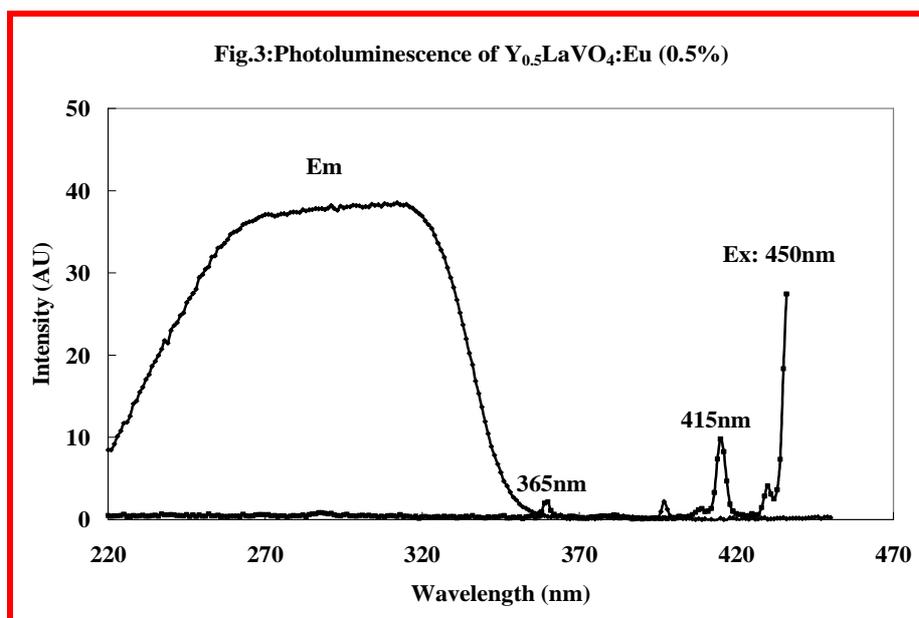
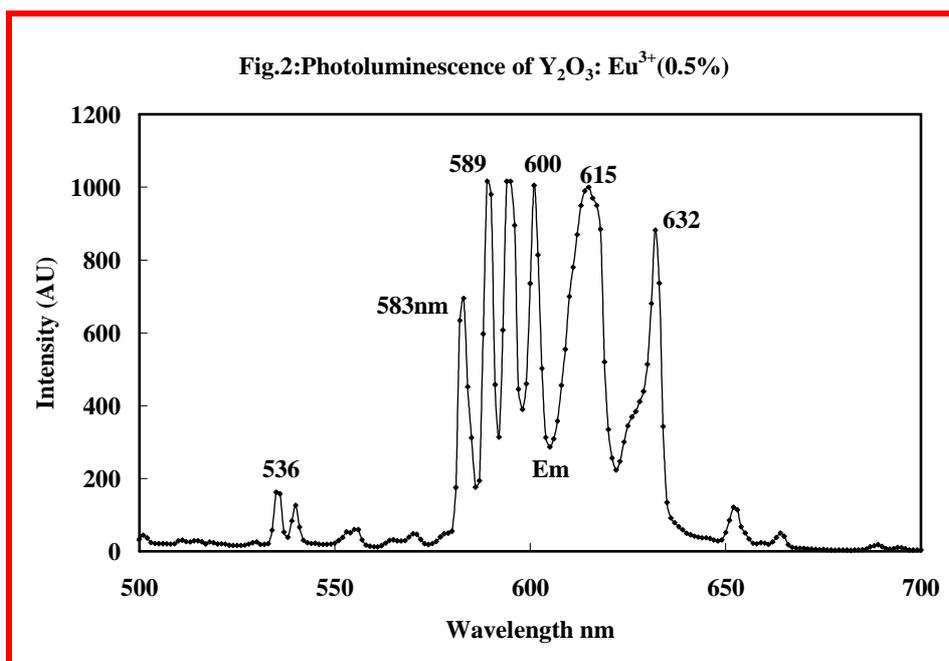


Figure.2. shows is the photoluminescence spectra of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (0.5%) being excited with 254 nm. The excitation of the material with 254 nm wavelength generates the emissions at 536, 583, 589, 594, 600, 615 and 632 nm. The intensity of the emission peak at 536 nm is as low as five times as compared to 583, 589, 594, 600, 615 and 632 nm peaks. The PL emissions at 583, 589, 594, 600, 615 and 632 nm are very sharp in intensity. When excited with 254nm normally the Eu^{3+} -activated Y_2O_3 gives strong emissions at 594, 611 and 617nm. But in the present investigation as many as eight transitions are observed. The possibility of contamination of unwanted impurities is also ruled out from EDXRF studies presented in fig.4.

Figure.3 shows the photoluminescence spectra of $\text{Y}_{0.5}\text{LaVO}_4:\text{Eu}$ (0.5%) being excited with 450 nm, the excitation spectra also contains 415nm line which is not able to emit any luminescence in the visible region. The excitation of the material with 450nm wavelength generates a strong and broad emission in UV region i.e. 240 to 300 nm in addition to another small emission peak at 365nm. The PL emission of $\text{Y}_{0.5}\text{LaVO}_4:\text{Eu}$ is interesting in nature as it displays up-conversion phenomena.



The color requirement in TVs and PDPs is primarily the red. From figure.1 it is to be observed that the intensities of 594 and 611 are same indicating that the phosphor formation is in single phase. As per literature Europium activated $Y(PV)O_4$ is an efficient red emitting phosphor that is currently used in PDPs due to its high QE persistence characteristics and reduced saturation. As it is reported $YPVO_4$ also displays the PL lines at 595, 611 and 617 when excited with 147 nm with intensity ratio 1:3:5.

Europium activated yttrium oxide is an efficient red emitting phosphor that is currently used in fluorescent lamps (High Pressure and low Pressure) as well as a red component in plasma

display devices. The Eu^{3+} -activated yttrium oxide is also being used as lamp phosphor since three decades. Less intense emission peak at 594 nm assigned to the $^5D_0 \rightarrow ^7F_1$ transition may help to improve the color purity in PDP application. As it was reported in $LaPO_4:Tm$, PL

emission at 291, 348 and 362nm was observed on excitation with 147 and 173nm. These emissions are assigned to ${}^1I_6 \rightarrow {}^3H_6$, ${}^1I_6 \rightarrow {}^3H_4$, ${}^1D_2 \rightarrow {}^3H_6$. But in any Eu doped phosphors, this type of PL is not observed to the best of our knowledge.

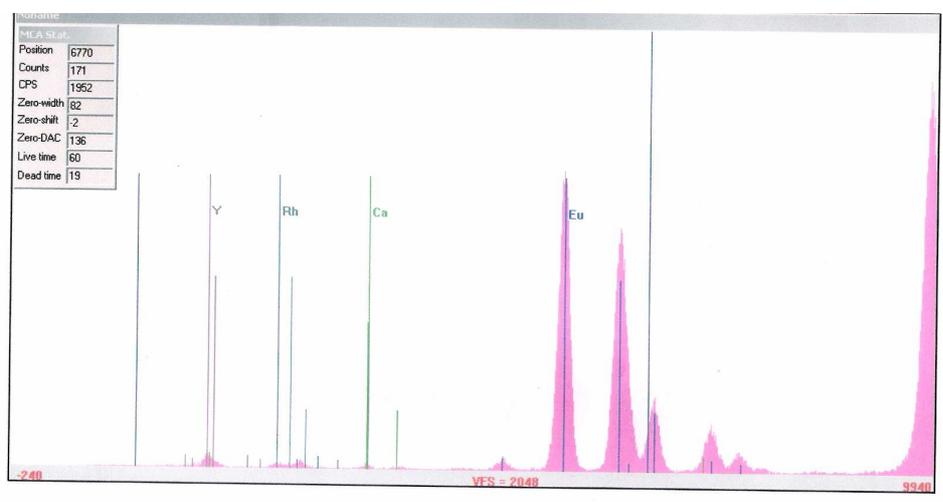


Fig.4: EDXRF of $Y_2O_3:Eu$

Table: 1: Photoluminescence Peak Emission wavelengths and Peak Intensities

Sr. No.	Sample Chemical formula	PL Emission Peak Wavelength (nm)	PL Emission Peak Intensity (AU)
1	$YPVO_4:Eu^{3+}$ (Ex: 254nm)	365, 540, 561, 594, 611	95, 143, 41, 1016, 1000
2	$Y_2O_3:Eu^{3+}$ (Ex: 254nm)	536, 583, 589, 594, 600, 615, 632	157, 634, 980, 999, 1004, 1000, 850
3	$Y_{0.5}LaVO_4:Eu$ (Ex :450nm)	254-320	35

Rao R.P reported a number of luminescence lines due to ${}^5D_J \rightarrow {}^7F_J$ of Eu^{3+} in BAM:Eu. It is reported that the emissions from 5D_2 and 5D_1 are quenched with an increase in the concentration of Eu^{3+} which is due to a cross-relaxation process, (${}^5D_J \rightarrow {}^5D_0$) (${}^7F_0 \rightarrow {}^7F_J$). The photoluminescence emission in the vicinity of 600 nm is due to the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$ which is insensitive to the site symmetry. The emission around 610-630 nm is due to the electric dipole transition of ${}^5D_0 \rightarrow {}^7F_2$ induced by the lack of inversion symmetry at the Eu^{3+} site and is much stronger than that of the transition to the 7F_1 state. Luminescent Eu^{3+} ions in commercial red phosphors such as YVO_4 , Y_2O_3 and Y_2O_2S occupy the sites that have no inversion symmetry. The strong emission is due to the electric dipole transition is utilized for practical applications. As per Blasse and Brill, if the Eu^{3+} site has inversion symmetry then the electric dipole emission is weak and the magnetic dipole transition becomes relatively stronger and dominates.

Considering a model where Charge Transfer Site (CTS) is a combination of $4f^7$ electrons plus a hole, one finds that the resulting spin multiplicities should be 7 and 9. It is the former state that affects optical properties related to the 7F_J state by spin-restricted covalency. The intensity ratio luminescence from ${}^5D_0 \rightarrow {}^7F_2$ and from ${}^5D_0 \rightarrow {}^7F_1$ decreases with increasing CTS energy sequentially as reported. These results suggest that higher CTS energies reduce the strength of the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ in Eu^{3+} .

The wavelength positions of the emission bands depend very much on hosts, changing from the near UV to the red. This dependence is interpreted as due to the crystal field splitting of the 5d level. With increasing crystal field strength, the emission bands shift to longer wavelength. The luminescence peak energy of the 5d-4f transitions of Eu^{2+} and Ce^{3+} are affected most by crystal parameters denoting electron- electron repulsion.

Sharp-line luminescence at 366 nm due to an f-f transition and having a lifetime of milliseconds is observed when the crystal field is weak so that the lowest excited state of $4f^7$ ($6P_J$) is lower than the $4f^6 5d^1$ state.

Europium activated yttrium, gadolinium borate $[(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}]$ is an efficient red emitting phosphor that is currently used in PDPs due to its high QE persistence characteristics, and reduced saturation. In general, the luminescence (emission) lines at 593, 611, and 627 nm correspond to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (orange red) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (red) transitions of Eu the peak end intensity of each red line (593, 611, and 627 nm) depend on the Eu and Gd concentrations. For lamp applications all three lines at 593 nm (orange), 611 nm (red), and 627 nm (red) are acceptable. But in the case of displays, specifically for TV applications, it is preferable to have more of the red. In these phosphors, the intensity of the orange line in the 582-600-nm wavelength range arising from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ in the wavelength range 600-645 nm is stronger.

CONCLUSION

Eu^{3+} shows the strongest emission at 615 nm and it is due to the electric dipole ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition arising from the noncentro symmetric structure of the host lattice. Sharp-line luminescence at 366 nm due to an f-f transition which is observed when the crystal field is weak so that the lowest excited state of $4f^7$ ($6P_J$) is lower than the $4f^6 5d^1$ state. The observed PL emission at 240 to 300 nm in $\text{Y}_{0.5}\text{LaVO}_4:\text{Eu}$ is concluded as up-conversion phenomena. This may be assigned to any one of the following transitions ${}^1\text{I}_6 \rightarrow {}^3\text{H}_6$, ${}^1\text{I}_6 \rightarrow {}^3\text{H}_4$, ${}^1\text{D}_2 \rightarrow {}^3\text{H}_6$.

Acknowledgements

Dr. K. V. R. Murthy is thankful to DAE/BRNS for sanctioning a research project on DREBP.

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